LONG LIFE Na/NiCl₂ CELLS

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ABSTRACT

The premature capacity failure of Ni/NiCl₂ secondary cells due to agglomeration of nickel particles on the surface of the NiCl₂ cathode is prevented by addition of a minor amount, such as 10 percent by weight of a transition metal such as Co, Fe or Mn to the cathode. The chlorides of the transition metals have lower potentials than nickel chloride and chlorinate during charge. A uniform dispersion of the transition metals in the cathodes prevents agglomeration of nickel. The additives do not effect sintering. The addition of sulfur to the liquid catholyte is expected to further reduce agglomeration of nickel in the cathode.

13 Claims, 3 Drawing Sheets
Fig. 1.
LONG LIFE NA/NICL₂ CELLS

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected not to retain title.

TECHNICAL FIELD

The present invention relates to high temperature rechargeable sodium-nickel chloride cells, and more particularly, this invention relates to new cathodes providing longer life sodium-nickel chloride cells.

BACKGROUND OF THE INVENTION

New types of electrical energy storage devices are needed to power electronic devices, electric vehicles and to smooth peak power demands on electric utilities. Some promising devices are based on the use of a solid electrolyte separator such as ceramic, beta alumina solid electrolyte (BASE).

STATEMENT OF THE PRIOR ART

Since the discovery in 1962 that the material β'-alumina was a good sodium ion conductor, several studies were made on its use as solid electrolyte separator in various battery systems with liquid sodium as anode. The interest for many years has been focused on sodium-sulfur battery, which has many attractive features such as high density, high rate discharge capability permitted by a good (comparable to aqueous electrolytes) ionic conductivity of β'-alumina solid electrolyte (BASE) at high temperatures and long cycle life and negligible self discharge. However, there are certain difficulties associated with the use of sodium-sulfur battery. In particular, due to the highly corrosive nature of sulfide melts, material selection for the current collector in the positive electrode is very critical and limited to a few possible choices. Also, there is a likelihood of BASE degrading in polysulfide melts. Further, the inherent violent reaction between liquid sodium and liquid sulfur demand a rather sophisticated design of the battery to circumvent the safety problem in the event of failure of the solid electrolyte ceramic.

A new class of high temperature, sodium rechargeable batteries based on transition metal chlorides as positive electrodes have emerged in the last decade. These systems are similar to the sodium-sulfur batteries in terms of anode half cell and the (high) energy densities. In addition, the use of solid metal chloride cathodes in basic chloraluminate melts results in several significant advantages, including lower operating temperatures, improved safety and high reliability. Excellent performance characteristics have been demonstrated with both Na/FeCl₃ and Na/NiCl₂ systems in small and large cells as well as in batteries.

However, a problem associated with the use of NiCl₂ is an agglomeration of the electrode particles causing a premature failure in the cycle life.

Addition of elemental sulfur alleviates this problem almost completely. Sulfur, however, is rather aggressive to the cell components causing corrosion problems similar to those in Na/S cell. Additionally, sulfur also affects the stability and reversibility of NiCl₂ at high concentrations. A non sulfur additive with the beneficial effects of sulfur is needed.

Adendorff and Coetzee teach adding 0.1 to 10 weight percent of transition metals other than Ni, Fe, Co, Cr or Mn to an active cathode so that the transition metal does not become chlorinated during charging.

The closest reference is Meintjes, et al. who discloses an active cathode substance for a Na/Cu cell comprising Fe, Ni, Co, Cr, Mn and mixtures thereof. It could be argued that Meintjes generally discloses Ni cathode comprising Ni with Co, Mn or Fe.

Bugga, et al. disclose a method of preparing a cathode in which a matrix of a metal nobler than the cathode metal is present.

Wright discloses coating a cathode current collector with graphite. Bones, et al. disclose Na-FeCl₃ cells.

STATEMENT OF THE INVENTION

The present invention relates to a non-sulfur additive to the nickel chloride cathode that prevents premature failure due to agglomeration of the electrode particles. The additive is not corrosive and has no effect on the quality of the sintered electrodes. A uniform dispersion of the additives in the cathode matrix prevents agglomeration of the nickel particles, thus retaining the morphology/capacity of the electrode. Furthermore, the additives utilized in the invention are more compatible than sulfur without posing any corrosion problems to the positive current collector (usually nickel) since the current collector is thermodynamically stable toward the additives.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a Na/NiCl₂ cell according to the invention;

FIG. 2 are a set of discharge curves of 2 Ah NiCl₂ electrodes with no additive, with 10% by weight percent Co, Mn or Fe; and

FIG. 3 is a set of curves showing variation of capacity of 2 Ah NiCl₂ electrodes with no additive or with 10% by weight percent Mn or Fe.

DETAILED DESCRIPTION OF THE INVENTION

Agglomeration of nickel particles on the surface of the electrode is prevented in accordance with the invention by the addition of a minor amount of a transition metal such as manganese, cobalt or iron having a lower potential than nickel to a sinterable mixture of nickel and sodium chloride to form a cathode for a sodium-nickel chloride electrochemical cell. The transition metal is present in an amount from 1 to 25% by weight of the cathode, preferably from 5 to 15% by weight of the cathode. The transition metal forms a chloride during charge of the cell preventing agglomeration of nickel particles at the electrode. The added transition metal chloride can participate in the cell reactions, thus contributing to the energy density of the cell. The combination of addition of a transition metal and sulfur may provide synergistic results.

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The anode current collector can take the form of a cylindrical or U-shaped metal tube such as stainless steel and the cathode current collector is preferably a sintered NiCl₂, usually fabricated as a dense microcrystalline sintered electrode containing a uniform dispersion of 1 to 25% by weight of a transition metal having a lower potential than nickel and being capable of reversible chlorination in the cell. The solid electrolyte is preferably a thin film of beta alumina which is a sodium ion conductor. Beta alumina and beta⁺-alumina or their mixtures are members of the class of materials known as solid electrolytes or fast ion conductors. These materials have ionic conductivity much larger than their electronic conductivities and thus act as electrolyte as well as separator. Beta⁺-alumina solid electrolyte (BASE) has a higher sodium conductivity than Beta alumina and is usually fabricated as a dense microcrystalline sintered ceramic. It is inert to reaction with elemental sodium at temperatures as high as 1300K. Its Na⁺ conductivity at 300°C is 0.4 ohm⁻¹ cm⁻¹.

The solid electrolyte can assume different configurations such as a flat barrier film or the solid electrolyte can be provided in cylindrical form. The surface can be planar or corrugated. The solid electrolyte usually utilizes a fairly thin film, typically having a thickness from 0.01 to 0.2 cm, generally around 0.1 cm.

The liquid catholyte comprises a mixture of salts of Group I and Group III metals which is molten at the operating temperature of the battery. The molten salt is preferably a Group I metal salt and can be a mixture of Group I and Group III metal salt such as a sodium tetrachloroaluminate (NaAlCl₄). The molten salt is preferably maintained basic by saturating with NaCl. The ratio of NaAl:AlCl₄ is preferably 1:1.

Referring now to FIG. 1, a battery cell comprises an outer cylindrical tube having a flange, suitably formed of a conductive, corrosion resistant metal such as stainless steel. A BASE tube is supported within the outer tube. The heater is connected to a variable power supply, controller. The anode current collector is the BASE tube. The cathode current collector is the BASE tube for receiving body. The BASE tube is connected to the BASE tube. The catholyte undergoes chlorination within the cathode current collector and is in contact with the body of molten sodium and a cathode current collector is in contact with the catholyte. The catholyte comprises a mixture of salts of Group II and Group IV metals which is molten at the operating temperature of the battery. The molten salt comprises a mixture of salts of Group II and Group IV metals which is molten at the operating temperature of the battery. The molten salt is preferably maintained basic by saturating with NaCl.

The liquid catholyte comprises a mixture of salts of Group II and Group IV metals which is molten at the operating temperature of the battery. The molten salt comprises a mixture of salts of Group II and Group IV metals which is molten at the operating temperature of the battery. The molten salt is preferably maintained basic by saturating with NaCl. The ratio of NaAl:AlCl₄ is preferably 1:1.

The current collector/electrode was constructed with a catholyte tube placed inside the SS tube and the cathode half cell. The columnar volume between the SS tube and the beta tube contained enough sodium to make the cells cathode limited. The electrodes of the beta tube were filled with sodium tetrachloroaluminate fused salt electrolyte. The sintered NiCl₂ electrode containing 10% Co, Mn or Fe immersed in the molten salt acted as the positive electrolyte. For the fabrication of the NiCl₂ electrode, INCO nickel powder type 255 (3 micron) was used. Sodium chloride obtained from Aldrich was preheated and pulverized to get a particle size less than 100 micron. All the cell fabrication and testing operations were carried out in an argon-filled glove box. Cell cycling was performed by Macsym system developed in-house. Morphological studies on the cycled electrodes were made using scanning electron microscopy. All the experiments were carried out at a temperature of 275°C, unless specified otherwise.

The NiCl₂ electrodes were fabricated by a cosintering of fine powders of Ni and NaCl mixed in the mole ratio of 3:1 and containing a uniform dispersion of 10% by weight of Co, Mn or Fe. On formation, one third of the Ni would thus be chlorinated, with the rest of the Ni acting as its grid. The electrodes could also be made by loose sintering, simply by filling the beta alumina tube with the electrode powders and producing sintered-like structure during initial charge. However, such electrodes would not permit any postmortem analysis unless the beta tubes are crushed. For the present study, therefore, the electrodes were pressed before sintering for ease of dismantling after cycling, while focusing on high electrode porosity.

The first batch of the electrodes were fabricated in prismatic or cylindrical configuration at a compaction pressure of 10,000 psi. The electrodes were obtained as fine powders. These electrodes would not permit any postmortem analysis unless the beta tubes are crushed. For the present study, therefore, the electrodes were pressed before sintering for ease of dismantling after cycling, while focusing on high electrode porosity.

The sintering of the electrode was carried out in an inert (argon) atmosphere at temperatures slightly below melting point of NaCl (801°C C.) for a period of 2 hours. In subsequent experiments, the sintering was carried out for only 15 min and in a reducing atmosphere (3% hydrogen).

2 Ah cells were fabricated and tested with no additive and with 10 weight percent of Co, Mn or Fe. These cells were cycled between 2.0 and 3.0 V vs. Na⁺/Na⁺. These cells have been typically charged at C/20 (or C/40) and discharged at C/10 rate. The capacity of the standard cell started falling sharply from 12th cycle and a reached a plateau value of 0.6 Ah (about 50% of the initial value) within 25 cycles. It is important to note that the failure of the cell appeared to be a hindered charging process. The dis-
NaCl is known to be a slow process. The charging process in the cell without additive, the electrode appears to have hardended during cycling, possibly due to agglomeration. It was found to be difficult to disassemble the electrode from the beta tube, whereas the electrode containing transition metal additives appeared powdery and could be easily removed. Scanning electron micrographs reveal that there is a considerable agglomeration in the electrode during cycling in the absence of transition metal in SEM micrographs of the NiCl₂ electrode before cycling (i.e. after sintering), after 60 cycles in sulfur-free electrolyte, after 50 cycles 2 Ah cell with 2% S and after 40 cycles in 3 Ah cell with 2%, respectively. The grain is increased from an initial value of 15 μ to 50-60 μ during cycling in the cell without additive.

Referring now to FIG. 2, Discharges curves of 2-Ah "loose sintered" NiCl₂ electrode in the electrolyte are shown as: (A) with no additive; (B) with 10 wt. % cobalt; (C) with 10 wt. % manganese; and (D) with 10 wt. % iron. Cells of Ah capacity and containing 10% Fe, Co or Mn as additives to the cathode were cycled and compared with the standard (without additive) cell (FIG. 2). The plateaus due to cobalt and iron chlorides occur at -50 mV and 250 mV less than of Ni, respectively. Manganese, on the other hand, would not undergo any reversible electrochemical reaction on the potential range studies.

Referring now to FIG. 3, variation of capacity during cycling at 10-h rate of 2-Ah "loose-sintered" NiCl₂ electrode in the electrolyte are shown as: (A) with no additive; (B) with 10 wt. % cobalt; (C) with 10 wt. % manganese; and (D) with 10 wt. % iron. Cells of Ah capacity and containing 10% Fe, Co or Mn as additives to the cathode were cycled and compared with the standard (without additive) cell (FIG. 3). As may be seen from FIG. 3, cells with the metal additives exhibit better capacity retention than the standard cell. Besides, the additives also undergo reversible electrochemical reaction in the potential range of 2.0-3.0 V, thus contributing to the cell capacity and energy density, which otherwise would have decreased. The cell with cobalt failed prematurely, possibly due to a failure of the solid electrolyte. The internal resistance values obtained from AC impedance are 0.23, 0.34, 0.17 and 0.22 m for the standard cell and the cells with Co, Fe and Mn additives respectively.

Transition metal additives, according to the invention, are found to have no adverse effect on the quality of the sintered structure. Since the potentials of the corresponding chlorides of the transition metals is lower than that of NiCl₂, there is chlorination of these metals during charge, thus forming mixed chloride cathodes. A uniform dispersion of these additives in the cathode matrix prevents agglomeration of nickel particles while retaining the morphology/capacity of the electrode. Furthermore, these additives are more compatible without posing any corrosion problems to the positive current collector (usually nickel), since nickel is thermodynamically stable towards the transition metals.

Though the beneficial effect of the transition metals reducing agglomeration is not a pronounced as with sulfur, a synergistic effect on agglomeration of nickel can be expected in a cell having a NaCl₂ electrode containing 1-25% by weight of a transition metal and a basic chloroaluminate electrolyte containing 0.1 to 5% by weight preferably 0.5 to 1.0 percent by weight of sulfur.

Furthermore, since the transition metal additives are less corrosive than sulfur, the cell containing the combined additives should have longer cell life.

The high temperature rechargeable sodium-nickel chloride cells of the invention are useful in applications requiring long cycle life, high energy and power densities such as electric vehicles, load leveling and space applications.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

We claim:
1. An electrode for a Na/NiCl₂ secondary battery comprising NiCl₂ containing a dispersion of from 1 to 25 percent by weight of particles of a transition metal having a lower potential than nickel.
2. An electrode according to claim 1 in which the transition metal reversibly chlorinates under the electrochemical condition of the cell.
3. An electrode according to claim 2 in which the transition metal is selected from the group consisting of Co, manganese and iron.
4. An electrode according to claim 3 in which the transition metal is present in an amount from 5 to 15 percent by weight.
5. An electrode according to claim 4 in which the transition metal is present in an amount of about 10 percent by weight.
6. An electrode according to claim 1, in which particles of nickel, the transition metal and sodium chloride are sintered to form said electrode.
7. A rechargeable Na/NiCl₂ cell comprising in combination a first body of molten sodium; a second body of molten basic aluminate salt; a ceramic separator which transports sodium ions between said bodies disposed between and separating said bodies; an anode connected to the first body; and a cathode immersed in the second body said cathode comprising nickel chloride containing a dispersion of a minor amount of particles of a transition metal having a lower potential than nickel.
8. A cell according to claim 7 in which the transition metal is present in the cathode in an amount from 1 to 25 percent by weight.
9. A cell according to claim 8 in which the transition metal reversibly chlorinates during charge-recharge cycling of the cell.
10. A cell according to claim 9 in which the transition metal is selected from the group consisting of cobalt, manganese and iron.
11. A cell according to claim 7 in which the second body includes from 0.1 to 3 percent by weight of sulfur.
12. A cell according to claim 11 in which the second body contains from 0.5 to 1.0 percent by weight of sulfur.
13. A cell according to claim 7 in which the cathode is formed from a sintered mixture of particles of nickel, the transition metal and sodium chloride.